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*Published in:*  
Energy Procedia

*Link to article, DOI:*  
[10.1016/j.egypro.2014.11.115](https://doi.org/10.1016/j.egypro.2014.11.115)

*Publication date:*  
2014

*Document Version*  
Publisher's PDF, also known as Version of record

[Link back to DTU Orbit](#)

*Citation (APA):*  
Gaspar, J., Thomsen, K., von Solms, N., & Fosbøl, P. L. (2014). Solid formation in piperazine rate-based simulation. *Energy Procedia*, 63, 1074-1083. <https://doi.org/10.1016/j.egypro.2014.11.115>

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GHGT-12

## Solid formation in piperazine rate-based simulation

Jozsef Gaspar<sup>a</sup>, Kaj Thomsen<sup>a</sup>, Nicolas von Solms<sup>a</sup>, Philip Loldrup Fosbøl<sup>a,\*</sup><sup>a</sup>Technical University of Denmark, Department of Chemical Engineering, Center for Energy Resource Engineering, Soltofts Plads, 2800, Kgs. Lyngby, Denmark**Abstract**

Piperazine is a promising solvent for reducing CO<sub>2</sub> emissions. It can be applied for the post-combustion capture process and it has limited degradation and fast kinetics. However, precipitation and slurry formation still represent a challenge for the PZ-CO<sub>2</sub>-H<sub>2</sub>O system from an operational point of view but also from a modeling perspective.

The present work develops a rate-based model for CO<sub>2</sub> absorption and desorption modeling for gas-liquid-solid systems and it is demonstrated for the piperazine CO<sub>2</sub> capture process. This model is an extension of the DTU CAPCO<sub>2</sub> model to precipitating systems. It uses the extended UNIQUAC thermodynamic model for phase equilibria and thermal properties estimation. The mass and heat transfer phenomena is implemented in a film model approach, based on second order reactions kinetics. The transfer fluxes are calculated using the concentration of the dissolved species since the piperazine is deactivated when present as solid. It is assumed that solid-gas reactions are slow compared to normal liquid side reactions.

In the current work, the formation of solids is described in an equilibrium approach, assuming instantaneous formation of hydrates such as PZ·6H<sub>2</sub>O, PZ·½H<sub>2</sub>O, and anhydrous PZ.

The simulation of a 100t/hr post-combustion capture plant outlines that 5 % solid reduces the CO<sub>2</sub> capture rate with 13%. Therefore, it demonstrates that an accurate description of the precipitation phenomenon is essential for realistic and accurate modeling.

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Peer-review under responsibility of the Organizing Committee of GHGT-12

**Keywords:** CO<sub>2</sub> post-combustion capture; piperazine; rate-based modeling; slurry formation and solid precipitation;

**1. Introduction**

Sustainable energy infrastructure development is a key challenge of our society. The power supply and demand patterns are continuously changing, but they are still rooted in fossil fuels. In order to reach the Zero CO<sub>2</sub> Emission policy, carbon capture has to be integrated with power production. Consecutive scale-up, validation and verification have to precede the deployment of a large scale industrial capture plant.

Several capture technologies exist at different levels of maturity. The piperazine (PZ) based CO<sub>2</sub> post-combustion capture process is the focus of this work. Piperazine and blends of piperazine with potassium salts are being suggested as innovative candidates for developing the CO<sub>2</sub> capture business. Piperazine presents several advantages over the base case MEA solvent such as low degradation and high reaction rate [1].

Precipitation is a process challenge. At room temperature solid is formed above 2 molal (20 wt.%) piperazine. The risk of precipitation is high especially in lean solutions, at process start-up during solvent mixing [2], or in the condensing reflux

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sections of the stripper. It could trigger a shut-down of the plant. These potential hazardous scenarios have to be identified in order to minimize the risk of equipment clogging.

A few works deal with developing rate-based models for piperazine and ammonia [3-5]. There is no popular rate-based model for CO<sub>2</sub> post-combustion process simulation which addresses the issue of precipitation. The growing interest for systems with solid formation calls for more realistic models. Precipitation must be included in the description of transfer phenomena and in the calculation of the equilibrium composition. One might note that the solidified components, e.g. PZ, NH<sub>4</sub>HCO<sub>3</sub> do not react with CO<sub>2</sub>. For example, when piperazine precipitates it leads to lowered absorption capacity, for example if 10 % of a 4.5 molal PZ solution precipitates then the concentration drops to 4.05 - 4.25 molal, depending on the type of the solid formed. Thus, less CO<sub>2</sub> can be consumed by the reaction at the same loading, and the driving force for CO<sub>2</sub> absorption decreases. Solid PZ behaves as an inert. Therefore solid-liquid phase change is important from a modeling point of view.

The present work describes a method for precipitating rate-based modeling. A hybrid CO<sub>2</sub> capture model is proposed and applied using a case of a 4.5 molal piperazine solution. It is an extension of the DTU CAPCO2 model [6] to gas-liquid-solid systems. It consists of a core thermodynamic engine and an accurate rate based model.

The focus is on evaluating the effect of solid formation on absorption capacity. It demonstrates that an accurate description of the precipitation phenomena as well as of thermodynamics, kinetics and mass transfer are fundamental for consistent and correct process modeling.

### Nomenclature

app	system without precipitate
b	bulk
$C_k^{ph}$	Molar concentration of component $k$ in phase $ph$ (mol/l)
$D$	Diffusivity coefficient (m <sup>2</sup> /s)
$E$	Enhancement factor
$E_{\infty}^*$	Instantaneous enhancement factor
$Ha$	Hatta number
$i$	interface
$k_2$	second order reaction rate constant (m <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
$k_L$	Liquid side mass transfer coefficient (m/s)
$L$	liquid mol flow rate (mol/s)
$n_i^{solid}$	Dissolution respectively precipitation rate (mol/sec)
real	system including solid-liquid equilibria
$T$	Temperature (K)
$x_k$	mol fraction of component $k$ (mol/mol)
$y_k^b$	Interface to bulk concentration ratio of component $k$
$y_k^i$	Bulk to interface concentration ratio of component $k$

## 2. A hybrid CO<sub>2</sub> capture model for gas-liquid-solid systems

The hybrid model is built on the core of the DTU CAPCO2 rate-based model called hCAPCO2. It uses the extended UNIQUAC thermodynamic model for the phase equilibria and thermal properties estimation [7]. The mass and heat transfer fluxes are determined in a film-theory approach, using the General Method (GM) model [8]. It is a second order kinetics based enhancement factor model.

The CAPCO2 differential equation system was previously described [6,9]. hCAPCO2 is formulated as a boundary value problem with fixed inlet conditions. The gas stream composition, temperature and molar flow are specified at the bottom while the liquid stream characteristics are specified at the top of the column. Equilibrium is assumed reached instantaneously between the solid and the liquid phase. Therefore, the composition of the solid phase is determined from the liquid phase using the extended UNIQUAC equilibrium calculations.

The precipitated solid is not present in the liquid phase and it is not free to react with dissolved CO<sub>2</sub>. Precipitation can be imagined as apparent removal of the active components, e.g. PZ, NH<sub>3</sub>, H<sub>2</sub>O from the solution. Consequently the solutions with less PZ will absorb less CO<sub>2</sub>. Therefore, the real concentration of the liquid phase needs to be considered in the transfer flux calculation. The concentration of the dissolved piperazine,  $x_{PZ}^{real}$  respectively water,  $x_{H_2O}^{real}$  is back-calculated from the initial concentration,  $x_i^{app}$  using the precipitated amount,  $n_i^{solid}$ , as shown in (1) and (3). Note that PZ forms hydrates, 1 mol of PZ can take away half to 6 moles of water. The type of hydrate depends on the composition and temperature of the system. The liquid mol fraction of CO<sub>2</sub> increases when PZ precipitates, according to eq. (2). Moreover, the total liquid mol flow also changes and it is calculated according to (3).

$$x_i^{real} = \frac{x_i^{app} L^{app} - n_i^{solid}}{L^{real}}, \text{ where } i = \text{PZ}, \text{H}_2\text{O} \quad (1)$$

$$x_{\text{CO}_2}^{real} = \frac{x_{\text{CO}_2}^{app} L^{app}}{L^{real}} \quad (2)$$

$$L^{real} = L^{app} - \sum_j n_j^{solid} \text{ where } j = \text{PZ}, \text{PZ} \cdot 6\text{H}_2\text{O}, \text{PZ} \cdot \frac{1}{2}\text{H}_2\text{O} \quad (3)$$

In (1) to (3), “*real*” refers to the composition respectively flow rate of the system excluding solids while “*app*” indicates total composition, assuming no precipitate.

### 3. Vapor-liquid-solid equilibrium for the PZ-CO<sub>2</sub>-H<sub>2</sub>O system

#### 3.1. The extended UNIQUAC thermodynamic model

The extended UNIQUAC thermodynamic model is used in the description of the vapour-liquid-solid equilibrium (VLSE). It is a Gibbs excess energy model which applies the thermodynamic  $\gamma$ - $\phi$  convention. It is used for liquid phase activity coefficients while the SRK equation gives the gas phase non-idealities.

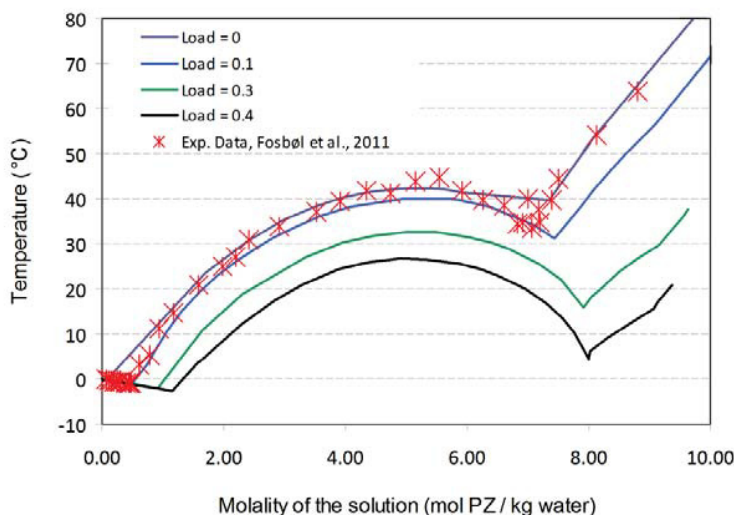
The extended UNIQUAC model was developed from the well-known UNIQUAC model by adding a Debye-Hückel term to correct for the electrostatic interactions between the ions in the liquid. A detailed description of the equation system and derived properties of the Gibbs excess model was previously given [10]. The method for VLSE calculation is presented by Thomsen et al. [7]. The fitting of the parameters were performed against a large database at Center for Energy Resources Engineering and applied in numerous CO<sub>2</sub> capture related projects, like the chilled ammonia capture process [3], or the novel ammonia capture process [11], etc. The parameters regressed for the system containing piperazine CO<sub>2</sub> are used in the present work to account for the interactions between the ions and for the interactions between molecules [12].

#### 3.2. Equilibrium calculation in the PZ-CO<sub>2</sub>-H<sub>2</sub>O system

The solid liquid equilibrium (SLE) phase diagram for the PZ-CO<sub>2</sub>-H<sub>2</sub>O system is shown in fig. 1. The curves represent the temperature at which PZ start to precipitate. The solid free operational range corresponds to the area above the curves. It highlight that 1.6 molal PZ can be dissolved at 20 °C and mixing of the fresh solvent without CO<sub>2</sub> has to be performed at higher temperature, especially for concentrated piperazine. If more than 8 molal solution is needed, then the solution must be heated above 45 °C to avoid precipitation. Unloaded PZ forms PZ·6H<sub>2</sub>O hydrates up to 45 °C at 4 molal. Adding more PZ will dissolve the solid and above 7 molal it precipitates as PZ·½H<sub>2</sub>O. Moreover, above 10 molal it solidifies as a mixture of solid PZ·½H<sub>2</sub>O and anhydrous PZ. The same behavior is shown by Fosbøl et al. [2].

Fig. 1 illustrates that the temperature at which PZ precipitates decreases with loading and it shows how the SLE curve has a local maximum in the concentration range 4 to 6 molal and it sharply increases above 9 molal. In the absorber unit, the loading of the solution is lowest at the column top and it increases towards the bottom as it absorbs CO<sub>2</sub>. A typical lean loading of an absorber is around 0.3 and 0.7 for a rich solvent. Fig. 1 shows that a 0.3 mol CO<sub>2</sub>/mol PZ solution dissolves completely above 33 °C up to 9 molal. The SLE curve moves up when loading decreases. A 0.1 mol CO<sub>2</sub>/mol PZ lean solution dissolves completely above 40 °C up to 8 molal and above 70 °C up to 10 molal. The SLE curve shifts down to 28° C for a 0.4 loaded solution.

Conclusively the analysis of the PZ-CO<sub>2</sub>-H<sub>2</sub>O system indicates that hydrates may form in the top part of an absorber. It is demonstrated that solids may form at 45 °C and below during solvent mixing and below 35 °C in lean solutions. The risk of equipment clogging is decreasing with loading. A 0.4 loaded solution will not precipitate above 30 °C. However, the temperature is increasing significantly above 8 molal, indifferent of the loading, as shown in fig. 1.

Fig. 1. SLE diagram for PZ-CO<sub>2</sub>-H<sub>2</sub>O system

#### 4. Simultaneous mass transfer and reaction modeling

The present work uses a general method (GM) enhancement factor model to determine the mass transfer rate, based on second order kinetic considerations. GM is a model which describes the intensification of the transfer phenomena in a reactive solvent like PZ compared to a physical solvent. To minimize the uncertainties related to the rate constant value, a new improved correlation is developed here using several experimental and empirical dataset discussed below. The analysis revealed discrepancies between various rate constant therefore a new improved correlation was developed here.

Derks et al. [13] proves that CO<sub>2</sub> and PZ can react according to various mechanism, however only the PZCOO<sup>-</sup> carbamate, (4) and the (PZCOO<sup>-</sup>)<sub>2</sub> bicarbamate, (5) forming reactions are important. They concluded that the reaction between CO<sub>2</sub> and PZ is overall second order and it behaves first order with respect to the reactants.



*B* is any base present in the solution, i.e. PZ, PZCOO<sup>-</sup>, PZH<sup>+</sup>, H<sub>2</sub>O or OH<sup>-</sup>. This kinetic is commonly used for primary and secondary amines.

Moioli and Pellegrini [5] pointed out that the bicarbamate forming reaction, eq. (5) has little influence on the behavior of the absorption column. According to Dang and Rochelle [14], the value of the kinetic constant for eq. (5) can be set to 25% of the forward rate constant  $k_{2,\text{PZCOO}^-}$ , eq. (4). It has to be mentioned that experimental data is not available for  $k_{2,\text{PZ}(\text{COO}^-)_2}$ . Therefore, the total second order rate constant is  $k_2 = 1.25 k_{2,\text{PZCOO}^-}$  where  $k_{2,\text{PZCOO}^-}$  is the reaction rate constant for eq. (4). A similar approach was adopted by Moioli and Pellegrini [5].

Fig. 2 shows the natural logarithm of the second order rate constant as function of inverse of temperature. In this figure, points represent experimental measurements while lines corresponds to empirical correlations [13,15-20]. It can be seen in fig. 2 that most of the experiments were carried out between 15 and 40 °C. Only Sun et al. [16] and Ume et al. [17] present data for temperatures up to 60 °C. Moreover, the covered PZ concentration range is fairly small, the highest concentration being 1 molar PZ. The summarized experimental values in fig. 2 were obtained using wetted wall column [15,16,20], stirred cell [13,18] and stopped flow experiments [17,19].

The analysis of available second order reaction rate constant values [13,15-20] substantiates the discrepancies, as shown in fig. 2. It demonstrates that measurements as well as correlations differ especially at temperatures below 50 °C, the most relevant temperature range for absorption. Note that the rate constant cannot be directly measured and it has to be back-calculated, for

example from CO<sub>2</sub> partial pressure measurements in the wetted-wall column experiments. Derks have shown that the use of different enhancement factor models result in differences between the calculated rate constants, especially when the reaction between CO<sub>2</sub> and PZ shifts from the pseudo-first order regime to the intermediate regime [13]. Therefore, a general valid enhancement factor model is essential for the determination of correct  $k_2$  value. Other possible source of the discrepancies between rate constants might be the applied experimental method and the range of the covered piperazine concentration.

The approach of the present work is to develop a new correlation, accounting for more measurements and correlations.

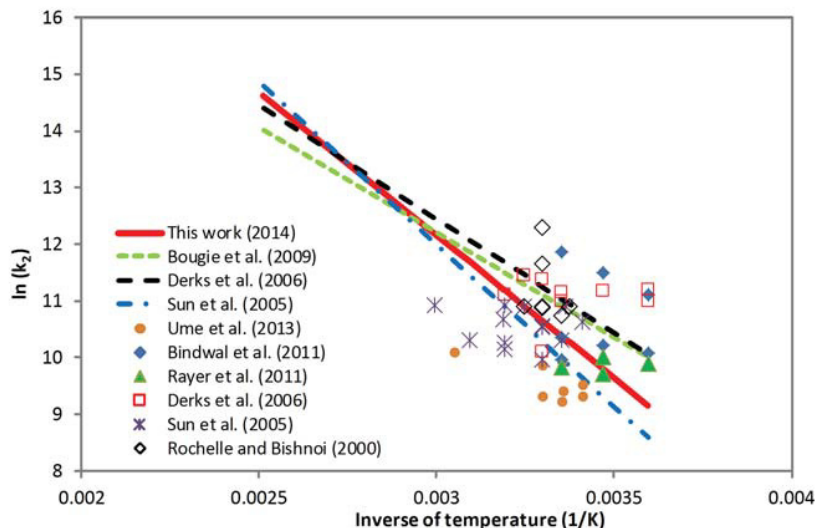


Fig. 2. Second order kinetic constant for aqueous CO<sub>2</sub>-PZ system according to different empirical (lines) and experimental (points) sources

Equation (6) gives the expression of the revised second order rate constant in m<sup>3</sup>/mol.s. It was obtained by fitting the parameters of an Arrhenius type equation to experimental and empirical data. Note in fig. 2 that the developed expression, eq. (6) fits the average of all the data. The absolute average deviation between experimental and calculated values is 6.86%.

$$k_{2,PZCOO^-} = 7.3376 \cdot 10^{10} \exp\left(\frac{-5054.34}{T / K}\right) \quad (6)$$

The simultaneous reaction and mass transfer is described using the enhancement factor approach. The enhancement factor is a relative factor which describes the intensification of the transfer phenomena by a reaction. In the present work, the GM model for second order kinetics is implemented. It is a film theory based enhancement factor model which relies on the overall reaction:



The GM model for the PZ-CO<sub>2</sub>-H<sub>2</sub>O system consist of equations (8) and (9). The solution of this equation system can be obtained iteratively since it is an implicit non-linear model with two unknowns,  $E$  and  $y_B^i$ .

$$E = 1 + (E_\infty^* - 1) \frac{1 - y_{PZ}^i}{1 - y_{CO_2}^b} \quad (8)$$

$$E = Ha \sqrt{y_{PZ}^i} \frac{1 - y_{CO_2}^*}{1 - y_{CO_2}^b} \quad (9)$$

where the dimensionless composition of the gas,  $y_{CO_2}^b$ , respectively liquid,  $y_{PZ}^i$  is defined in (10) to (12). The ratio of the interface to bulk concentration of CO<sub>2</sub> respectively PZ indicates the driving force for mass transfer. For example,  $y_{CO_2}^b=1$  shows that the net transfer rate is zero and its value is decreasing with the increase of the driving force for absorption.

$$y_{CO_2}^b = \frac{C_{CO_2}^b}{C_{CO_2}^i} \quad (10)$$

$$y_{PZ}^i = \frac{C_{PZ}^i}{C_{PZ}^b} \quad (11)$$

$$y_{PZ(COO^-)_2}^i = 1 + \frac{C_{PZ}^b}{C_{PZ(COO^-)_2}^b} (1 - y_{PZ}^i) \quad (12)$$

The rate expression enters the GM mass transfer model through the Hatta parameter, which is defined in eq. (13).

$$Ha = \frac{\sqrt{k_{2,PZCOO^-} C_{PZ} D_{CO_2}}}{k_L} \quad (13)$$

Assuming that the reaction reaches equilibrium in the film, the composition of A-component which will be in equilibrium with its interface concentration is:

$$y_{CO_2}^* = y_{CO_2}^b \left( \frac{y_{PZ(COO^-)_2}^i}{y_{PZ}^i} \right)^2 \quad (14)$$

The maximum limit of CO<sub>2</sub> mass transfer enhancement is given by the instantaneous enhancement factor. It corresponds to a case of infinitely fast reaction, when CO<sub>2</sub> is consumed immediately by the reaction with PZ. This relation enters the expression of the enhancement factor, eq. (8) and according to the two-film theory is:

$$E_{\infty}^* = 1 + \frac{2D_{PZ}}{D_{CO_2}} \frac{C_{PZ}^b}{C_{CO_2}^i} \quad (15)$$

The behavior of the GM model was extensively tested for CO<sub>2</sub>-MEA-H<sub>2</sub>O system by Gaspar et al. [8]. The study shows the excellent accuracy of the model for a broad temperature and loading ranges and demonstrates that the model predicts the two-film model within 2% accuracy.

## 5. Results and discussion

The present work shows that precipitating systems are challenging not only from an operational perspective but also from a modeling point of view. In this study, the hCAPCO2 model is applied for a large scale CO<sub>2</sub> absorber calculation using aqueous piperazine. The focus is on the boundaries where precipitation occurs in relatively small percentage, up to 6% solid of the liquid phase. The importance of solid formation in rate-based modeling is highlighted in terms of the difference between the CO<sub>2</sub> partial pressure calculated with the traditional CAPCO2 and the hCAPCO2 model. The results for the MEA process are also shown to validate the model on a qualitative base. In addition, the hybrid CAPCO2 model is compared with experimental data from Plaza [21]. The experimental campaign covers wide PZ concentration range, however the loading of the solution was kept relatively high for all of the runs which might be due to safety considerations.

### 5.1. Validation of the hybrid carbon capture model

The hCAPCO<sub>2</sub> model is compared with experimental CO<sub>2</sub> absorption measurements to analyze the behavior of the model for a wide piperazine concentration range, from 4 to 9 molal PZ. The present study considers all of the data reported by Plaza [21] for the “November 2008” campaign. It has to be noted that the flue gas was not saturated in water and the humidity of the gas feed is back-calculated. Therefore, the water condensation/evaporation rate might be biased leading to discrepancies between the measured and calculated temperatures. In addition, the difference between the actual and calculated humidity influences the accuracy of the calculated mass transfer rate. The campaign was performed with approximately constant flue gas flow rate and the temperature of the lean solution was kept around 40 °C. The loading of the solution was varied between 0.25 and 0.38 mol CO<sub>2</sub>/2 mol PZ, according to Plaza [21]. The temperature of the flue gas was low (below 25 °C) compared to industrial cases and it was not saturated with water. The 12 mol % CO<sub>2</sub> gas feed was obtained by mixing cold air with pure CO<sub>2</sub>. In the current work the water content of the flue gas is determined with the extended UNIQUAC model assuming that a saturated air flow is mixed with pure CO<sub>2</sub> at specified pressure and temperature to match the 12 % CO<sub>2</sub> composition. The campaign was performed in an absorber with two sections of structured packing, each one of 3.05 m. The diameter of the column is 0.427 m. The liquid and gas phase temperature are measured at several places along the column and the loading of the feed respectively rich solution is determined by titration. Plaza claims that the accuracy of the absorber titrations are within ± 10% and the liquid side removal matches the gas side results within ±15%, except for runs 4 and 10 [21].

Fig. 3 shows the calculated CO<sub>2</sub> mass transfer rate against the measured absorption rate. It demonstrates the good agreement between the hCAPCO<sub>2</sub> model and the experiment. The absolute average deviation between the model and experiment is 8.68%. There seems to be two outliers for the 7 molal cases which might be due to the discrepancy between the measured and calculated humidity of the flue gas. Note that the inlet temperature of the flue gas for the two outliers is -5 °C and 22 °C. These values are situated in the extremities of the flue gas temperature range.

Fig. 3 outlines, that most of the calculated and measured values overlap, and the error between the model and experiment is not systematic. Some of the cases are a bit over- and others are under-predicted by the hCAPCO<sub>2</sub> model. However, all of the results are between the accuracy of the measurements. The results substantiate that the model is able to catch the effect of the PZ concentration on the absorption rate.

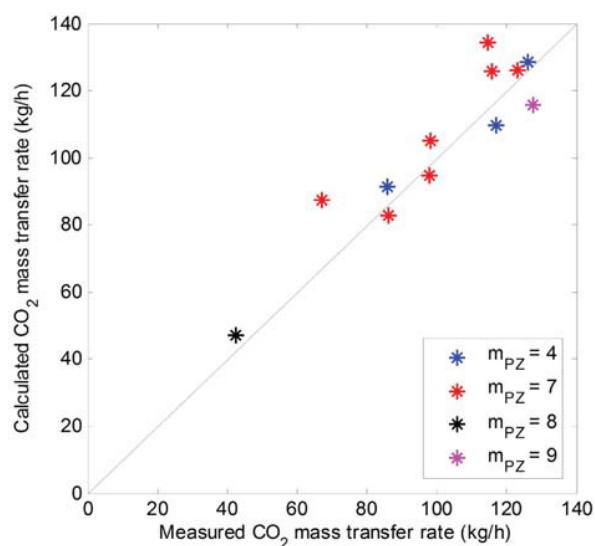


Fig. 3. Calculated CO<sub>2</sub> mass transfer rate versus measured transfer rate at four different PZ molalities

Similar conclusion can be reached by analyzing the agreement between the measured and predicted temperature profiles which are not shown. However, it has to be noted that the model generally over-predicts the temperature which might be due to the adiabatic column assumption. In addition, the accuracy of the measured values is also questionable. Moiola and Pellegrini [5] outlined that the temperature data do not show a unique temperature profiles, due to the fact that both, the gas and liquid phase have been measured but they were not differentiated.

It can be concluded that the hCAPCO<sub>2</sub> model behaves well for the CO<sub>2</sub>-PZ-H<sub>2</sub>O system and it can be used for CO<sub>2</sub> capture modeling. The extended UNIQUAC and the GM enhancement factor model with second order kinetics is a acceptable for



absorption process calculations. The hCAPCO<sub>2</sub> inherits the robustness and accuracy of the CAPCO<sub>2</sub> model and it extends to precipitating systems.

## 5.2. The effect of solid formation on the rate-based modeling

The change in the PZ solvent performance with respect to solid is investigated here. The absorption capacity of a 4.5 molal PZ solution is evaluated at two different CO<sub>2</sub> loadings and it is compared with the base case MEA solvent. The analysis reveals an unexpected change in the performance of the two solvents for the simulation scenario when the solid fraction is higher than 4 % solid PZ in the liquid. It has to be said that the equivalent loadings (mol CO<sub>2</sub>/mol alkalinity) and the concentrations of the PZ and MEA solutions are set equal to keep the systems comparable.

Two larger scale scenarios, 100 tone CO<sub>2</sub>/hr capacity absorber columns, are considered in the present simulation study. The flue gas is specific for a coal fired power plant with a capacity of 400MWe. We assume that the lean solution is available at 0.1 respectively 0.2 mol CO<sub>2</sub>/mol PZ loading and at relatively low temperatures, approximately 25 °C. Low loading and temperature values are chosen to push the system to precipitate. The aim of the present work is to investigate the effect of solid formation on the absorption capacity rather than to reproduce a real industrial case. However, this simulation scenario might correspond to CO<sub>2</sub> absorption with a mixture of fresh solvent and lean solution.

Fig. 4 and 5 show the simulation results for the two scenarios. In the present work, the CO<sub>2</sub> mol fraction along the column height, calculated with the hCAPCO<sub>2</sub> and the traditional CAPCO<sub>2</sub> model are given. The calculations for PZ and MEA are shown. The solid fraction of the liquid phase along the absorber height (red line) is included in fig. 4 and 5. It is calculated with the hCAPCO<sub>2</sub> model.

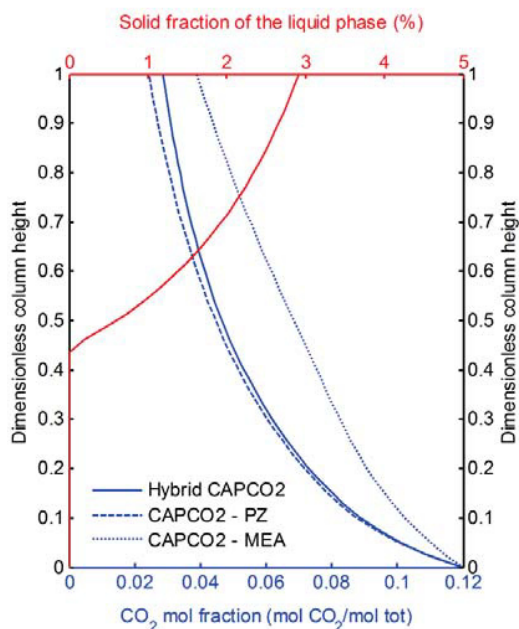


Fig. 4. CO<sub>2</sub> mol fraction along the column height with CAPCO<sub>2</sub> and hCAPCO<sub>2</sub> for a lean loading of 0.2 mol/mol

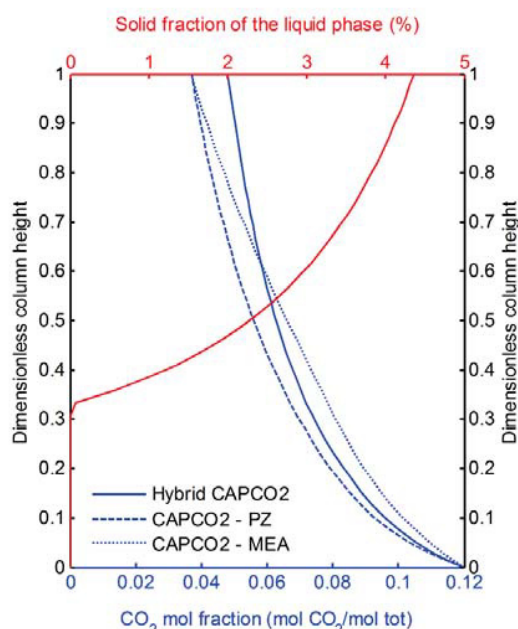


Fig. 5. CO<sub>2</sub> mol fraction along the column height with CAPCO<sub>2</sub> and hCAPCO<sub>2</sub> for a lean loading of 0.1 mol/mol

Fig. 4 emphasizes that the mol fraction of CO<sub>2</sub> calculated with the CAPCO<sub>2</sub> and the hCAPCO<sub>2</sub> model overlap for the 0.2 mol CO<sub>2</sub>/mol PZ scenario. A small difference between the two can be noticed at the top of the column, where the loading respectively the temperature of the liquid are the lowest. Note in fig. 4 that the solid fraction is decreasing exponentially from the top to the bottom of the column. The piperazine dissolves completely from the middle section of the column, when the loading reaches 0.27. As expected, MEA captures less CO<sub>2</sub> than PZ. The flue gas outlet CO<sub>2</sub> composition using PZ is 2.85 mol % while with MEA is 3.89%.

Fig. 5 shows the behavior of the model using 0.1 loaded solution. It demonstrates that the SLE phase change needs to be included in the absorber calculation. A solid fraction higher than 3% (mol solid/total mol) liquid results in the decrease of the solvent capacity. The precipitated PZ behaves as an inert and the solvent captures less CO<sub>2</sub>, as shown in fig. 5. The outlet gas

stream CO<sub>2</sub> composition is 1% lower considering precipitation than with CAPCO<sub>2</sub>. The hCAPCO<sub>2</sub> model estimates an outlet CO<sub>2</sub> concentration of 4.8 mol% while the traditional two-phase model gives 3.68%. The drop in the capture rate with the increase of the solid fraction is expected since the solid PZ does not react with CO<sub>2</sub> and it leads to the decrease of the driving force for absorption.

Fig. 5 captures a strange however rational phenomena. It shows that the 4.5 molal and 0.05 mol CO<sub>2</sub>/mol MEA loaded solution dissolves 13% more CO<sub>2</sub> than PZ. Based on the results, it is recommended to include the SLE phase change in the precipitating systems modeling. It is not enough to correct the values of thermal properties and partial pressures to system with solids. The real concentrations and fluxes needs to be used for accurate description of precipitating systems.

The hybrid model is a first step towards accurate modeling of absorption column with solid and slurry formation. It does not describe the size of the crystals but estimates the conditions with risk of clogging of the units. The hybrid model is a first of its kind gas-liquid-solid packed column model for CO<sub>2</sub> absorption and desorption.

It is expected that piperazine combined with organic bases are much more prone to precipitate and awareness should be taken when evaluating such systems. As shown in the present work, precipitation changes considerably the performance of the solvent and therefore solid-liquid phase change must be included in modelling.

## 6. Conclusions

It can be concluded that a hybrid capture model has been developed and demonstrated for piperazine CO<sub>2</sub> capture as a specific case. This model is able to predict the formation of solids. When amines are used for CO<sub>2</sub> capture, less attention is given to the solid-liquid equilibrium (SLE) phase change. Typical rate based models therefore do not consider the precipitation and slurry formation. The developed model for CO<sub>2</sub> absorption and desorption combines both equilibrium and a rate based model. Precipitation is predicted using the extended UNIQUAC thermodynamic framework, while the flue gas and solvent liquid phase is described by a rate based approach. The equations describing solid formation are integrated into the system of differential equations.

The thermodynamic framework, used for the vapor-liquid-solid equilibrium (VLSE) calculation, is based on a general electrolyte model, called the extended UNIQUAC model. It is consistent with previous works and modeling. This thermodynamic framework predicts the formation of various hydrates, PZ·6H<sub>2</sub>O, PZ·½H<sub>2</sub>O, anhydrous PZ, but also ice.

The thermodynamic analysis of the PZ-CO<sub>2</sub>-H<sub>2</sub>O system substantiates that precipitates might form in the top section of the absorber. It shows that solids form at 45 °C and below during solvent mixing and below 35 °C in lean solutions. The risk of precipitation is especially high for lean solution, in the concentration range 4 to 6 and above 8 mol PZ/kg H<sub>2</sub>O. Solid formation may also occur in the reflux section of the stripper, due to condensation.

The hybrid model is built on the core of the robust and accurate DTU CAPCO<sub>2</sub> rate based model. It includes the solid-liquid phase change in the estimation of the properties and parameters along the column. The developed model was validated against experimental data published by Plaza. The study shows that the prediction of the model is in the accuracy range of the experimental measurements.

An analysis revealed that 5 % solid reduces the CO<sub>2</sub> capture rate with 13%. Furthermore, it demonstrates that an accurate description of the precipitation phenomenon is essential for realistic and accurate modeling.

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